

Sorption Properties of Poly(styrene-*co*-divinylbenzene) Amine Functionalized Weak Resin

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ABSTRACT: The poly(styrene-*co*-divinylbenzene) amine functionalized weak resin was studied as adsorbent of heavy metal ions from an aqueous solution by using the Batch equilibrium procedure. The resin adsorbed Hg(II) 56% (0.56 mEq/g) at pH 2, and 45% (1.13 mEq/g) of U(VI), 38% (0.36 mEq/g) of Pb(II) at pH 5 from an aqueous solution containing 1 g/L of each metal ion. It did not adsorb Cd(II), Zn(II). The equilibrium time was achieved during the first hour. The maximum load capacity for Hg(II) was 0.8 mEq/g (75 mg)/g dry resin. It is possible to recover around 60% of the resin after the treatment with 1–4 M HClO₄ and HNO₃ of the loaded Hg(II) resin. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 80: 2123–2127, 2001

Key words: sorption; chelating resin; amino groups; metal ions

INTRODUCTION

The main application potential of chelating polymers is based on the possibility of achieving high selectivity of the materials for particular ions. Attempts have therefore been made to incorporate a vast number of chelating groups into polymer networks. Reviews cover many examples.^{1–6} Of the various common methods to prepare such chelate resins, by far the most common technique is the chemical modification of crosslinked polymers, and chloromethylated polystyrene crosslinked with divinylbenzene has served as the basic network in most of them.

The selective complexation of a targeted metal ion by a given ligand is an important objective for many applications, including catalytic,^{7,8} chromatographic,⁹ and metal ion recovery processes.^{10,11} The

ion-exchange reaction is an extremely versatile reaction, and one that is well suited to the complexation cations and anions through electrostatic binding. Ion-exchange resins are very important to metal ion complexation reactions due to their hydrophilicity, accessibility, and high capacity, but the synthesis of a polymer with a greater degree of selectivity would prove to be important to different applications. However, due to a wide range of materials and methods of synthesis is not surprising that the chelating exchanger's physical form may vary from rock-hard material to soft gel. The desirable properties of chelating exchangers are fourfold:¹¹ (1) high capacity for the metal(s) of interest; (2) high selectivity; (3) fast kinetics-rapid equilibration with metal-containing solutions; and (4) high mechanical strength and toughness of the exchanger particles. Unfortunately, the last two are competitive.

One of the most efficient and selective ligand groups is the amine group. The first report of the metal complex formation of a polymeric amine in the literature¹² concerned the binding of Cu(II) and Ni(II) by branched poly(ethyleneimine). Such complexes are highly soluble in water and can, in

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principle, be investigated by conventional solution chemistry methods. There are many reports in which some kind of interaction between polymeric amines and metal ions was observed.^{13–18} T. Saegusa et al. reported that Ni(II) and Cu(II) and several other metal ions bind to branched poly(ethyleneimine) with coordination number $n = 4$; nevertheless, Ni(II) forms complexes with $n = 6$ exclusively, and Cu(II) has coordination numbers $n = 4$ or 5, depending on pH.

In this article the binding ability to heavy metal ions of the poly(styrene-*co*-divinylbenzene) amine functionalized weak base resin by using the Batch equilibrium procedure is reported. The retention dependence on the pH, maximum load capacity, effect of the Hg(II) concentration, equilibrium time, and recovery of the resin are studied.

EXPERIMENTAL

Materials

Resin was supplied by Aldrich Chem. Co. Analytical grades of copper nitrate, cadmium chloride, mercury nitrate, lead nitrate, zinc nitrate, chromium nitrate monohydrate, uranyl acetate (Merck, Darmstadt, Germany) were used as received for metal sorption experiments.

pH Dependence for the Metal Ions

A typical equilibrium sorption experiment was carried out in a tube, applying 100 mg of resin of 10 mL of metal solution (from Cu(NO₃)₂, CdCl₂, Zn(NO₃)₂, Pb(NO₃)₂, HgNO₃, Cr(NO₃)₃, (CH₃COO)₂UO₂ of a known concentration. The pH was adjusted with dilute NaOH and HNO₃, depending on the metal to avoid precipitation. The suspension was agitated for 1 h at 25°C. The suspension was filtered off and the filtrate was diluted with distilled water. The metal ions, except uranyl ions, were analyzed by atomic absorption spectroscopy. To determine the maximum load capacity, a 250-mL beaker containing dry resin (1.0 g) and mercury nitrate solution (50 mL) (equivalent to 1.0 g mercury/L) were placed in a thermostatically controlled bath at 25°C. The mixture was shaken for 1 h. The aqueous solution was separated by decanting and filtration, and washed with distilled water. This process was repeated three times using the same resin. Mercury ions were determined by AAS, and the mercury ions

fixed in the resin was determined from the difference.

Determination of Desorption Properties of the Resin

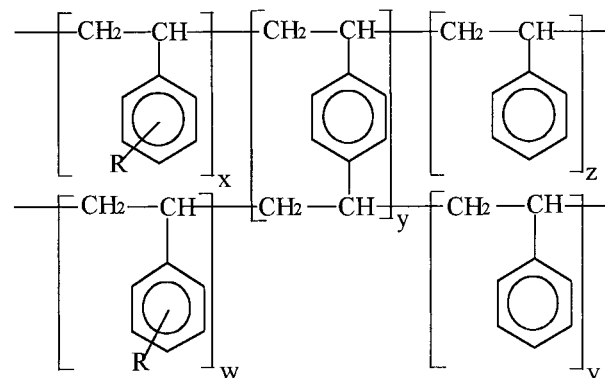
One hundred milligrams of dry loaded resin were shaken in a 20-mL flask with 10 mL of solutions of 1–4 M HClO₄, and 1–4M HNO₃. After 1 h the loaded sorbent was filtered off and washed with distilled water. The combined filtrates were analyzed for indirect determination of the amount of sorbed metal ion.

Equipments

The pH was measured with a digital Extech Microcomputer pH meter. The uranyl ions were determined on a CADAS 100 spectrophotometer. All the other ions were analyzed by atomic absorption spectroscopy by using a Perkin Elmer 3100 spectrometer. FTIR spectra were recorded with a Magna Nicolet 550 spectrophotometer. The thermograms of the resin and the loaded resin were recorded with a Thermoanalyzer STA 625 from Polymer Laboratories under N₂ with a heating rate of 10°C min⁻¹.

RESULTS AND DISCUSSION

The commercial poly(styrene-*co*-divinylbenzene) amine functionalized weak resin was used to study the analytical parameters by Batch equilibrium procedure of the following metal ions: Cu(II), Cd(II), Zn(II), Hg(II), Pb(II), Cr(III), and U(VI).



The fact that pK_a values of primary amines hardly changes at all as one changes the alkyl substituent from methyl to ethyl, isopropyl, or

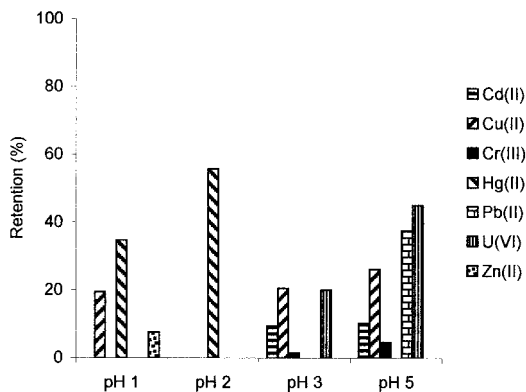


Figure 1 Batch sorption of metal ions by poly(styrene-co-divinylbenzene) amine functionalized resin at different pH; 100 mg of resin, 1 h shaking time.

tert-butyl gives the impression that the inductive effects predicted by these different substituents are identical. A considerable amount of data on the binding of amines and other bases to metal ions in the gas phase¹⁹⁻²¹ is available, which should allow a better analysis of such inductive effects.

The metal ion retention behavior was studied at different pH according to the water solubility of the metal salts. Thus, Hg(II) was studied only up to pH 2.

Figure 1 shows the effect of the pH on metal ion sorption. As pH is increased, the metal ions form more stable complexes with the polymer. At pH 2, Hg(II) is retained in 56% (0.56 mEq/g), but at pH 5, Pb(II) 38% (0.36 mEq/g) and U(VI) 45% (1.13 mEq/g). The order of affinity found at pH 5 was: U(VI) > Pb(II) > Cu(II) > Cd(II), Cr(III) and at pH 1 it was: Hg(II) > Cu(II) > Zn(II) > Cd = Cr(III) = Pb(II) = U(VI).

Uranyl complexation by amino ligands is highly dependent on the pH. Acid media, by causing the competition between H^+ and UO_2^{2+} , reduce the complexation of metal ion by the ligand. The H^+ UO_2^{2+} ion exchange in aqueous solution has been also studied in the material modified by *in situ* sorption and thermal polymerization of acrylic acid in low-density poly(ethylene) films. Fluorescence spectroscopy was used to observe the percentage of UO_2^{2+} exchange.²²

According to these results the following retention properties were carried out for mercury(II) and uranium(VI). The pH was not higher than 2 to avoid the precipitation of mercury salt.

The time required to achieve the equilibrium conditions is approximately 1 h, which can be considered relatively fast considering that the re-

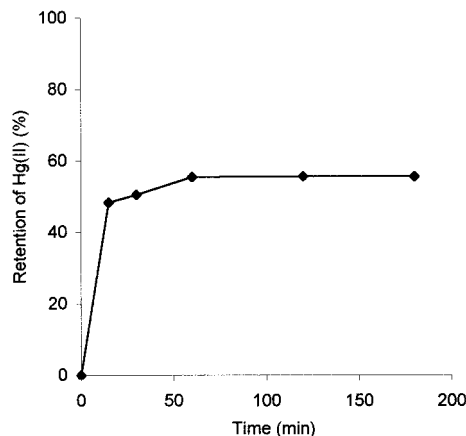


Figure 2 Batch sorption of mercury(II) as a function of time at pH 2, 100 mg of resin, 1 h of shaking time, 25°C.

action occurs in heterogenous phase (see Fig. 2). Sorption ability to Hg(II) is shown in Figure 3 as a function of the initial concentration of the metal ion at pH 2 after the batch contact with 100 mg of dry resin. The amount of Hg(II) ion adsorbed per unit mass of the resin increases the concentration from 0.25 to 1.0M, and then decreases up to 19.9M, keeping constant at about 40%. This would mean a partial saturation of the active sites available to bind mercury ions in this concentration range. It is remarkable that the affinity of the tertiary amino groups is not strong enough for mercury ions.

The maximum capacity of load for Hg(II) after three batch contacts of 1 g of dry resin with an aqueous solution containing 1 g/L in Hg(II) was 0.8 mEq/g (75.0 mg/g).

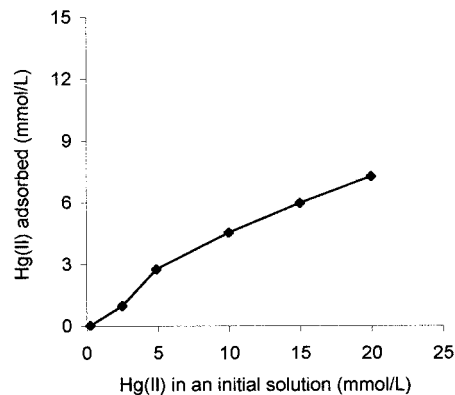


Figure 3 Batch sorption of mercury(II) as a function of the initial concentration in U(VI), at pH 2, 25°C, 100 mg of resin, 1 h of shaking time.

The selectivity sorption of Hg(II) from a binary mixture with U(VI) was carried out at pH 2. This binary mixture was selected due to both metal ions usually have a similar retention mechanism. Selectivity is given by the difference in distribution coefficients for different metal ions, and was determined according to the following equation:

$$S = \log Kd(\text{Hg}) - \log Kd(\text{U}),$$

where Kd is the distribution coefficient of the respective metal ions.²³

Kd

$$= \frac{\text{amount of the metal ion in the resin volume of the resin (mL)}}{\text{amount of the metal ion in the solution weight of the resin(g)}}$$

The distribution coefficient for mercury(II) and uranium(VI) are 150 and 83, respectively. Therefore, the selectivity, S , is 0.3. This sorption behavior is very similar to that observed for noncompetitive conditions. The relatively higher preference of the resin for the adsorption of Hg(II) may be attributed at least two factors, i.e., stability constant for complex formation and conformational requirements.

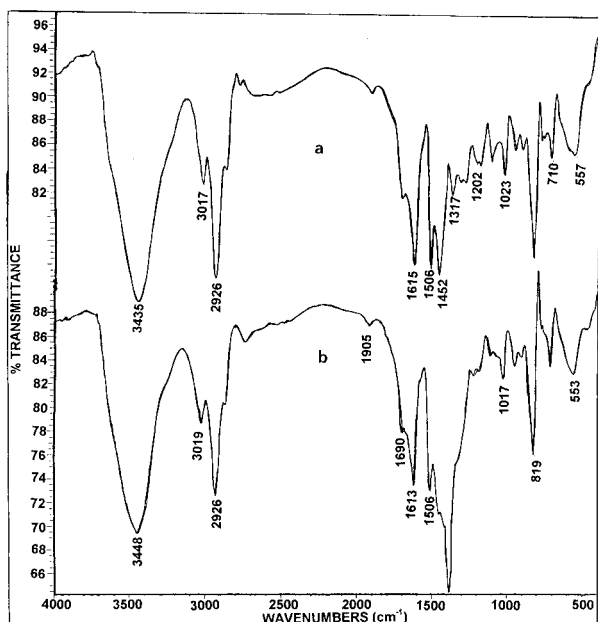


Figure 4 FTIR spectra of the (a) unloaded resin and (b) mercury(II) loaded resin.

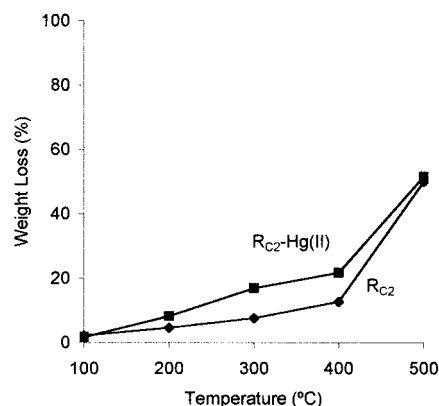


Figure 5 TGA under N_2 with a heating rate of $10^\circ\text{C min}^{-1}$ of (a) unloaded resin and (b) mercury(II) loaded resin.

The FTIR spectra of the unloaded resin shows, among other characteristic absorption signals (in cm^{-1}), at 3435 (N—H), 3017 (Csp^2), 2926 (C—H), 1506 (C—N), and the corresponding to the loaded with Hg(II), a shifting of the C—N signals and the presence of a strong absorption signal at 1382.7 cm^{-1} attributed to NO_3^- coming from mercury salt (see Fig. 4).

To determine the effect of Hg(II) adsorbed on the thermal stability of the resin, thermogravimetric analyses were carried out (see Fig. 5). The resin was loaded with mercury(II) at pH 2 according to maximum load capacity. There is no important effect of the the presence of metal ion on the thermal stability. In both materials the weight loss is lower than 52% at 500°C , and up to 300°C it is smaller than 17%. The weight loss of the loaded resin was relatively higher than that unloaded. In principle, the mercury ions would form basically intrachain complexes with the tertiary amino groups of the resin.

Desorption of Hg(II) ions from the loaded resin was studied with 1–4M HClO_4 and 1–4M HNO_3 solutions at 25°C by 1 h of shaking time. The final amount of mercury ions was determined by AAS and calculated by using the following expression:

Desorption rate:

$$\times \frac{(\text{amount of Hg(II) desorbed to the elution medium})}{(\text{amount of Hg(II) adsorbed on the resin})}$$

These media cannot efficiently destroy the amino–Hg(II) complex as being independent on the

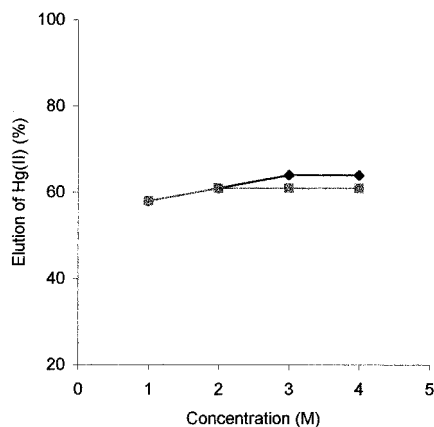


Figure 6 Desorption of mercury(II) from the resin by (a) HClO_4 , (b) HNO_3 , total amount loaded on 100 mg of resin, 1 h shaking time, 25°C .

concentration; the recovery was not higher than 61% (0.2 mmol of mercury ions) (see Fig. 6).

CONCLUSIONS

As pH is increased, the metal ions form more stable complexes with the polymer. The order of affinity changes with the pH. At pH 1 and 5, the highest affinity was observed for $\text{Hg}(\text{II})$ and $\text{U}(\text{VI})$, respectively. $\text{U}(\text{VI})$ showed a low affinity at pH 1. The amino resin adsorbed 0.56 mEq/g of mercury ions at pH 2, but did not adsorb $\text{Pb}(\text{II})$ or $\text{Zn}(\text{II})$. The intense absorption signal at 1382.7 cm^{-1} attributed to the nitrate group corroborates the sorption of mercury ions on the resin. After three batch contacts the sorption capacity was 0.8 mEq/g, demonstrating the partial saturation of the active sites to bind mercury ions. The nitric acid and perchloric acid allowed partially recover the resin by elution (approx. 60%) of mercury ions.

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